ORIGINAL RESEARCH

Anti-corrosion performance of waterborne Zn-rich coating with modified silicon-based vehicle and lamellar Zn (Al) pigments

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Abstract   In order to develop the eco-friendly Zn-rich coatings with higher corrosion resistance and lower pigment contents, several series of coatings were designed and manufactured employing lamellar Zn (Al) pigments mixed with silicone-acrylate emulsion modified inorganic silicate vehicle, and then were evaluated by conventional methods and the electrochemical method. The results indicated that the pigment contents reduced to approximate 25 mass% with lamellar Zn or (Zn and Al) pigments as substitute for spherical Zn pigments, and pigment mixtures were homogeneously dispersed due to silicone-acrylate emulsion moistening modification. Furthermore, the optimal coating had good coating properties (adhesion grade: one), acid

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resistance (lower mass losses) and anti-corrosive performance (improved corrosion potential and anodic passivation). The experimental results indicated that the modified lamellar Zn (Al) coating was suitable for large-scale spread and application on protecting steel structures in the hostile environment.

1. Introduction

Steels are the most popular and important structural materials in the world up to now. However, the problem of corrosion of structural steels must be considered during industrial applications. Surface coating on the steels is one of the effective protection methods, and zinc is a typical metal pigment widely used in anti-corrosion coatings, and the Zn-rich coating is considered as an effective coating for steel structures due to its more negative standard corrosion potential [1–3]. According to the nature of the paint vehicle, Zn-rich coatings are classified into two kinds i.e., organic and inorganic coatings [4]. Organic Zn-rich coatings usually contain organic solvents, such as benzene series and ethanol series, which are not compatible with ecological environment and they are harmful for human health [5]. In the inorganic-type coating, it is easy to realize the using of the water in the paint as the solvent. The waterborne inorganic Zn-rich coatings have been used for many years [6]. Since the waterborne coatings release almost no solvent fumes into the atmosphere, which is a considerable advantage given environmental restrictions [7,8], and they must be considered as one of the development tendencies of the eco-friendly paints.

At present, fine spherical Zn particles occupy a very big share in the waterborne inorganic Zn-rich paints. In order to guarantee the electrochemical protection of Zn pigments, a high pigment volume concentration ($C_{v,p}$) of Zn pigments is required, usually larger than 77% [9]. However, it is difficult to make homogeneous distribution of Zn pigments in the paint with such high $C_{v,p}$. In addition, the spherical zinc particle has a low surface area/weight ratio, thus they tend to separate or settle from the vehicle, leading to some serious coating defects [10].

Kalendova et al. [11] reported that the performances of the organic Zn-rich coatings were improved by using lamellar zinc pigments instead of the spherical ones. In comparison with the spherical zinc particle, the lamellar zinc pigment exhibited superior characteristics in the coatings [9]. The important advantage is that the lamellar zinc pigment exhibits a higher surface area/weight ratio which produces more effective electrical contact and lower current density in the protection process of the zinc-rich coating [12,13]. In addition, the lamellar zinc pigments have a good suspension property in vehicles, which makes the lamellar zinc pigments difficult to settle from the vehicle. Furthermore, the $C_{v,p}$ of the lamellar Zn-rich paint can be reduced dramatically, which brings better economic benefits.

In order to improve the corrosion resistance of the Zn-rich coatings, several investigation [14–18] have been carried out and the results showed that the corrosion rate of the coating can be decreased by using some lamellar aluminum pigments instead of the lamellar Zn pigments. For example, the Dacromet coating, which is a layer structure consisting of

lamellar Zn and Al pigments, exhibited consistent appearance and good corrosion resistance [19,20]. Panossian et al. [21] also reported that Zn-rich coating with certain content of Al pigments could afford better cathodic protection on the steel substrate. In addition, Feliu's reports showed that Al particles could obstruct the oxidation of zinc in the Zn-rich coatings [22,23].

These results give referential meaning for the waterborne inorganic Zn-rich coatings. In fact, it is a challenge to apply lamellar Zn and Al pigments dispersedly in the waterborne inorganic coatings. During the milling procedure of lamellar Zn or Al pigments, some wetting agents were added to make pigments separate more easily and improve the ability of the mill, which brings the low critical wetting surface tension of the lamellar pigments. In theory, if the surface tension of vehicle is lower than the critical wetting surface tension of pigments, when the pigments are wetted by the vehicle, the surface energy of pigments would decrease, thus the wetting process of pigments in the vehicle would occur spontaneously. In the waterborne inorganic paint, the surface tension of vehicle is higher than the critical wetting surface tension of lamellar Zn and Al pigments, which causes the pigments difficult to be well-dispersed and wet in this paint. In order to solve this problem, certain type of component with low surface tension should be added into the waterborne inorganic vehicle. Thus the modified vehicle could function with a relatively low surface tension, which is beneficial for the dispersity of the lamellar Zn and Al pigments in the paint. The combinations of a certain organic emulsion and an inorganic vehicle have both properties of their components [24].

According to the employing experiences of the organic Zn-rich coatings and Dacromet coating, the better performance can be expected when using lamellar Zn and Al mixture pigments in the waterborne inorganic paint. The effect of lamellar Al pigments used in the modified Zn-rich paint coating has not been reported. The aim of this work is to design and produce a new eco-friendly waterborne Zn-rich anticorrosion paint for steel parts, which will be mixed with modified silicon-based vehicle, lamellar Zn and lamellar Al pigments. Then, the physical characteristics, acid resistance, heat resistance, cathodic protection effect and corrosion resistance of the new coating on the steel substrate will be investigated.

2. Experimental

2.1. Preparation of the steel substrate and the modified vehicle

The steel Q235 plates with sizes of 30 mm × 30 mm × 2 mm were used as the substrates. The pretreatment of the steel substrate surface is essential to making high quality coatings, which strongly depends on the contamination of the surface.

In this work, the steel plates were degreased by hot alkaline soak, and sandblasted to Sa 2.5°.

The silica solution and the potassium hydroxide in a mass ratio of 10.7:1 were mixed by a motor stirrer in a thermostat water bath at 55 °C for 10 min, which was the inorganic potassium silicate vehicle. By adding silicone-acrylic emulsion into the inorganic vehicle and mixing for 40 min, the modified silicon-based vehicle was obtained. According to our previous works, the optimal mass fraction of the silicone-acrylic emulsion was 20% in the modified silicon-based vehicle.

2.2. Processing of the coatings

The lamellar Zn pigments in a mass fraction of 25% were added into the inorganic vehicle and stirred for a certain time, which was the unmodified Zn-rich paint (denoted by FZ paint). The lamellar Zn pigments in a mass fraction of 25% were added into the modified silicon-based vehicle and stirred, which was the modified Zn-rich paint (denoted by MFZ paint). The lamellar Al and lamellar Zn pigments in a mass ratio of 15:85 were mixed homogeneously in a container, and the mixed pigments in a mass fraction of 25% were added into the modified silicon-based vehicle and stirred, which was the modified Zn and Al paint (denoted by MFZA paint). The coating on the Q235 plate was made by the immersion method. The prepared Q235 plates were separately immersed into the three types of the paints for 10 s, and then removed from the paints and air-dried under the natural conditions.

2.3. Measurements of the coatings' performances

The weight per unit area of the coating was measured by the traditional dissolution method. The coating thickness was approximately calculated by the common density method. The adhesion of the coating to the substrate was estimated by using the scribe testing method according to the ISO 2409:1992. The acid resistances were tested by immersing the samples into a 0.3 mass% nitric acid solution, and the mass losses of the samples were measured separately after 7.5, 48 and 72 h.

The heat resistances of the coated samples were tested in a drying oven at 150 ± 3 °C for 3 h according to the Chinese Standard GB 1735-89. The qualified coating is free of discoloration, foreign particles, blisters, cracks and other defects after this test.

The corrosion resistance and cathodic protection effect were evaluated by the salt spray testing according to the ISO 7253-2002, and the samples of the coatings used were cut an "X" mark reaching to the steel base which was with 60° angle and 0.5 mm in width. The corrosion extent after 96 h in the 3.5 mass% NaCl solution was used to estimate the cathodic protection effect. The initial rusting time of the "X" mark was used to estimate the corrosion resistance of the coating. The samples coated by FZ and MFZ paints were also tested by an electrochemical method (potentiodynamic polarization) using an advanced electrochemical system of Princeton PAR-STAT2273. The effective surface area of the coated sample was approximately 1 cm². The electrochemical measurement was carried out in the chlorine solution (3.5 mass% NaCl solution) using a conventional three-electrode potentiostat. The potential was referenced against a saturated calomel electrode (SCE), and the counter electrode was a large platinum slice. The corrosion morphologies were observed by a JSM-5610LV scanning electron microscope (SEM).

3. Results and discussion

3.1. Effect of modified silicon-based vehicle

The thicknesses of the FZ and MFZ coatings by the dipping method were different, which were about 80 and 60 μm, respectively. The thickness of the dip coating is dependent on the viscosity and rheological properties of the paint, which lies on its components. For the FZ paint, in the waterborne potassium silicate vehicle, it is difficult to uniformly disperse the lamellar Zn pigments, which causes the viscosity of the FZ paint high and its rheological property poor. Therefore, the thickness of the FZ coating is large. But the case of the MFZ paint is different, in which the modified silicon-based vehicle was used, and the surface tension was reduced, thus the lamellar pigments could be well-dispersed. The dispersing time of Zn pigments in the modified silicon-based vehicle is only about 20 min. Compared with the FZ paint, the viscosity of the MFZ paint is lower and its flow ability is better. So, the thickness of the MFZ coating is lower than that of the FZ coating. The performances of the two coatings are listed in Table 1.

Table 1 shows that the MFZ coating has a stronger adherence to the substrate than the FZ coating. The modified silicon-based vehicle contains a silicone-acrylic emulsion, which reduces the brittleness of the silicate coating and improves adhesion indirectly. In addition, the duration time of the MFZ coating is longer than the FZ coating, which means that the MFZ coating has better cathodic protection effect than the FZ coating. This may attribute to the fact that the lamellar Zn pigments in the MFZ coating maintained electrical contact with each other, which was resulted from the well-dispersed pigments in the MFZ paint. In addition, the heat resistances of the FZ and MFZ coatings were better due to the superior high-heat resistance of the silicon-based material.

Fig. 1 shows the rusting morphologies of the two samples after 120 h immersion in the 3.5 mass% NaCl solution. It clearly shows that the FZ coating rusts seriously throughout the whole surface, as shown in Fig. 1(a), while the MFZ coating shows no obvious corrosion damage, as shown in Fig. 1(b).
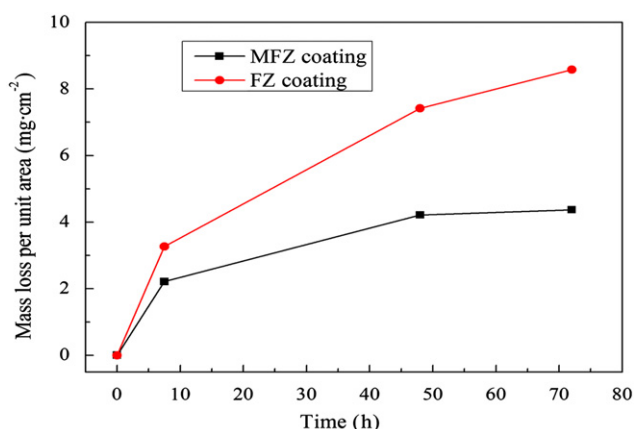
Fig. 2 shows the acid resistance of the FZ and MFZ coatings via mass loss per unit area as a function of immersion time in the 0.3 mass% nitric acid solution. The mass loss of the MFZ coating sample is smaller than that of the FZ coating sample during the whole exposure time. After 72 h immersion,

Table 1 Some performances of the FZ and MFZ coatings.

Type of coating	Adhesion grade	Initial rusting time (h)	Heat resistance
FZ	1	96	Unwounded
MFZ	0–1	120	Unwounded
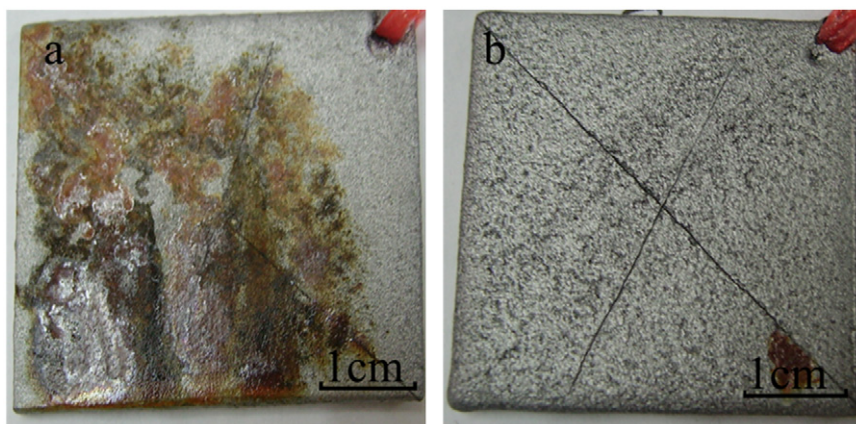
Fig. 1 Surface morphologies of the coatings after 120 h immersion in 3.5 mass% NaCl solution: (a) FZ and (b) MFZ coatings.
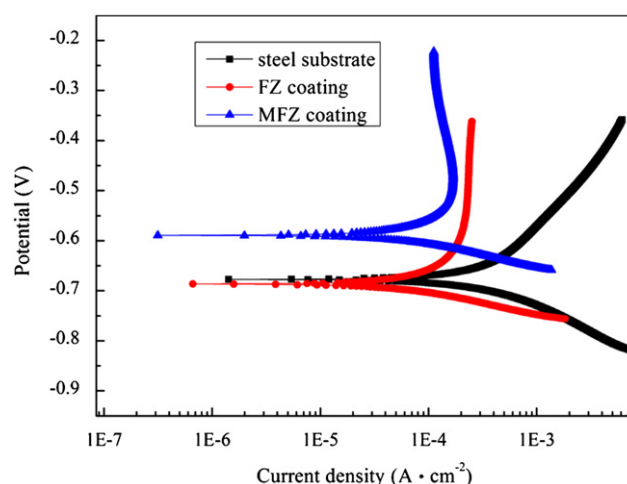

Fig. 2 Mass loss curves of the FZ and MFZ coating samples immersed in the 0.3 mass% nitric acid solution.

Fig. 3 Polarization curves for the steel substrate, the FZ and MFZ coating samples immersed in the 3.5 mass% NaCl solution for 30 min.

the mass loss of the MFZ coating sample was only half that of the FZ coating sample. Since the Zn pigments are chemically active, the Zn-rich coating is not resistant to the corrosive acid solution. However, the silicon-based Zn-rich coating gives improved acid resistance due to the highly chemical anti-corrosion properties of the silicate materials as a vehicle.

3.2. Polarization curves

Fig. 3 gives the polarization curves of the steel substrate for the FZ and MFZ coatings samples. The curves show that the cathodic polarizabilities of the three samples are similar, but their anodic polarizabilities are markedly different. Compared with the steel substrate, the anodic passivation of the FZ and MFZ coatings samples are remarkable, indicating that the FZ and MFZ coatings samples have lower anodic corrosion and better corrosion resistance. Meanwhile, the E_{corr} value of the MFZ coating sample is 100 mV more positive than that of the FZ coating sample, and the anodic polarization rate of the MFZ coating sample is larger than that of the FZ coating sample, indicating excellent passivity of the MFZ coating. To some extent, the more positive corrosion potential of the coating sample means that the corrosion process of the steel substrate is more strongly prevented by the coating. Due to the larger compactness, the MFZ coating prevents the

permeation of aggressive medium to the substrate, and makes higher corrosion potential. Thus more the positive corrosion potential and excellent passivity indicate, more the corrosion resistance given by the MFZ coating.

The above results demonstrate that the inorganic potassium silicate solution modified by the silicone-acrylic emulsion could improve pigments dispersion in the water-based paints. The rheological properties of the MFZ paint is better to form a continuous and compact coating, which gives a strong adhesion to the steel substrate, an improved acid and heat resistance, and excellent cathodic protection.

3.3. SEM observation

Fig. 4 illustrates the morphologies of the FZ coating before and after 1000 h immersion in the salt spray observed by SEM. It shows that a lot of large holes (about 100 μm) and a few of cracks can be found in the original coating surface. After corrosion test, those large holes are disappeared due to the stack of the corrosion production of the Zn pigments in the coating. However, small cracks amount on the coating increased clearly after corrosion test, which affects resisting the penetration of
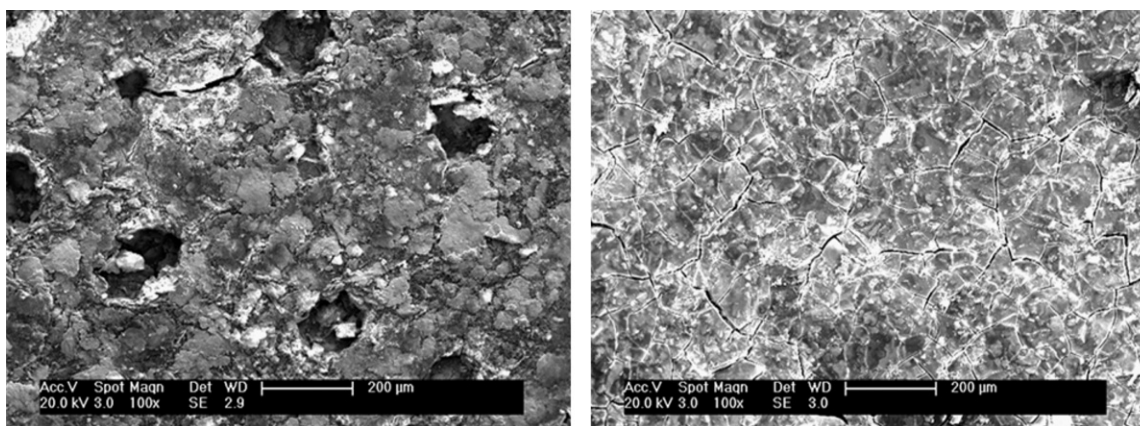
Fig. 4 SEM images of the original FZ coating (left) and its corroded coating exposed in the salt spray for 1000 h (right).
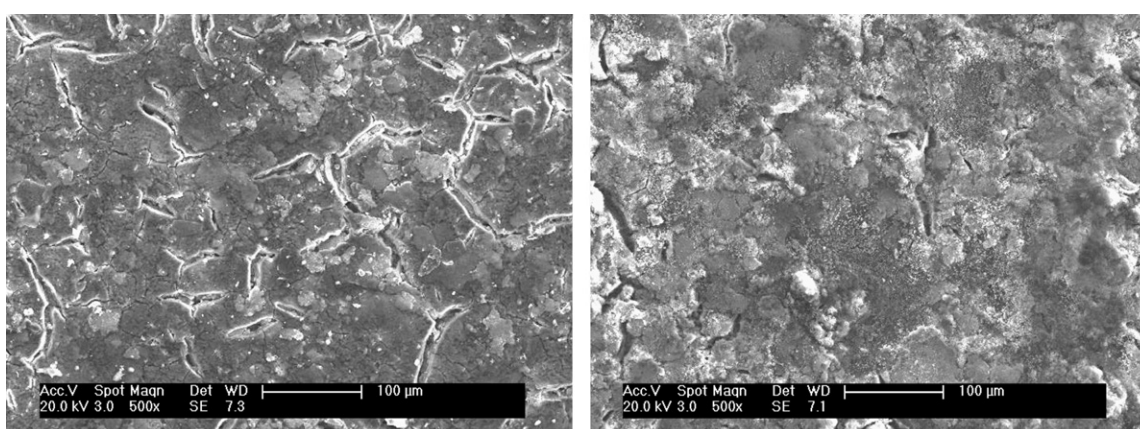

Fig. 5 SEM images of the original MFZ coating (left) and its corroded coating exposed in the salt spray for 1000 h (right).

aggressive medium. In FZ coating used unmodified vehicle, the Zn pigments were not well-dispersed and not completely encased by the vehicle, which causes the formation of large holes and big cracks. The exposed Zn pigments were highly susceptible to corrosion. Therefore, the corrosion resistance of the FZ coating was poor. The SEM morphologies of the MFZ coating samples before and after 1000 h immersion in the salt spray are shown in Fig. 5. It can be observed that on the original MFZ coating surface, there are many cracks but no holes. After the corrosion test, the cracks are clearly filled in by the corrosion products on the MFZ coating sample surface. Due to the improved flexibility, the MFZ coating did not increase the crack amount by the permeation of the aggressive medium.

3.4.   Effect of the lamellar Al-pigment addition on the coating

The thickness of the MFZA coating by the dipping method is about 60 μm, which is similar to that of the MFZ coating. Some performances of the MFZ and MFZA coatings samples are listed in Table 2. It clearly shows that the MFZA coating has exceptional performances. The initial rusting time of the MFZA coating sample is almost twice as long as that of the MFZ coating. Fig. 6 shows two photos of the coated samples: (a) MFZ coating and (b) MFZA coating. The Al powers are silvery and bright in color, which improve the brightness of the MFZA coating, as shown in Fig. 6(b). On the other hand,

Table 2   Some performances of the MFZ and MFZA coatings.

Coating	Appearance	Adhesion grade	Initial rusting time (h)	Heat resistance
MFZ	Silver gray	0–1	120	Unwounded
MFZA	Silvery	0–1	216	Better

the adhesion force of coating is more dependent on the vehicle of the paint than the pigments, so the MFZA coating also exhibits good adhesion similarly to the MFZ coating. In addition, due to the high heat resistance of the Al pigments and the modified silicon-based vehicle, the MFZA coating exhibits better heat resistance than that of the MFZ coating.

The initial rusting time of the MFZA coating sample is 216 h for immersion in the 3.5 mass% NaCl solution, which is longer than that of the MFZ coating sample. Fig. 7 presents the rusting morphology of the MFZA coating sample after immersion for 216 h. It clearly shows that no signs of corrosion exist on the metallic substrate of the MFZA coating sample. Due to the easy passivation of Al pigments in the MFZA coating, the current between the anodic coating and the cathodic steel base is decreased. Thus the MFZA coating gives longer-term cathodic protection than the MFZ coating.
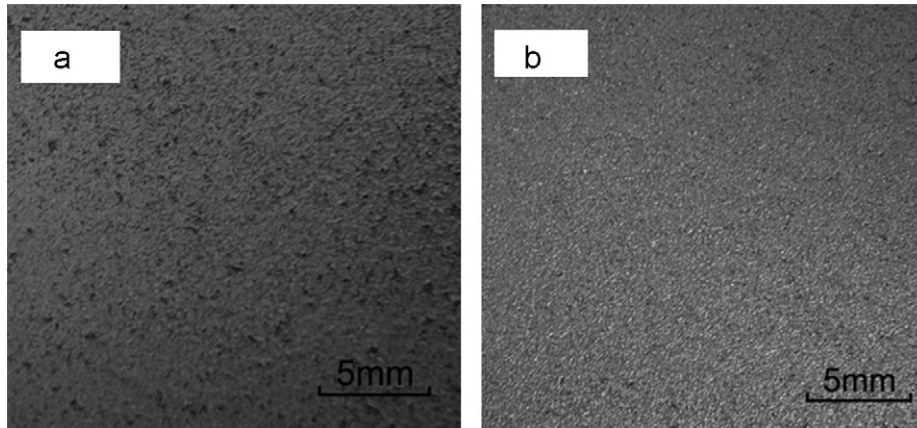
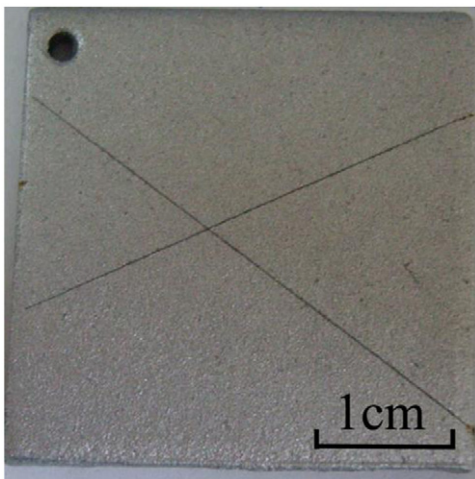Fig. 6   Surface morphologies of the two coatings: (a) MFZ and (b) MFZA.

Fig. 7   Surface morphology of the MFZA coatings after 216 h immersion in 3.5 mass% NaCl solution.

Fig. 9   Polarization curves for the MFZ and MFZA coating samples immersed in the 3.5 mass% NaCl solution for 30 min.

the MFZA coating sample is smaller than that of the MFZ coating sample during the whole immersion time. The improved acid resistance of MFZA coating results from the easy passivation of Al pigments in the acid solution.

Fig. 9 gives the polarization curves of the MFZ and MFZA coatings samples. The curves show that the anodic and cathodic polarizabilities of the two samples are similar, i.e. they run the similar corrosion dynamic behaviors. Compared with the MFZ coating, the anodic passivation current of the MFZA coatings samples is smaller. Thus the MFZA coating has lower anodic corrosion and better corrosion resistance. Meanwhile, the E_{corr} value of the MFZA coating sample is similar to that of the MFZ coating sample.

3.5. Performance comparisons between the MFZA coating and the traditional silicate spherical Zn coating

Table 3 lists the properties of the MFZA coating samples and the traditional silicate spherical Zn coating [25]. The pigment content of MFZA paint is significantly lower than that of the spherical zinc paint, which brings economic benefit. Due to the mixture of the Al powders in the pigment, the MFZA is glossier than the spherical Zn coating. Although the thickness of the MFZA coating is about 60 μm and thinner than that of the spherical Zn
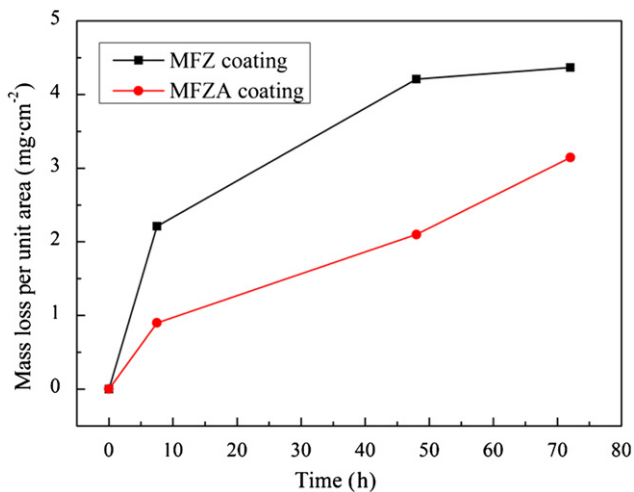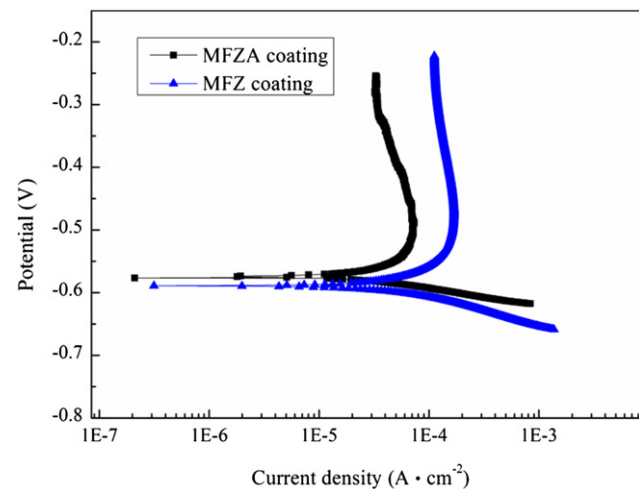

Fig. 8   Mass loss curves of the MFZ and MFZA coating samples immersed in the 0.3 mass% nitric acid solution.

Fig. 8 shows acid resistance of the MFZ and MFZA coatings via mass loss per unit area as a function of immersion time in the 0.3 mass% nitric acid solution. The mass loss of

Table 3 Properties comparisons between the MFZA coating and the traditional silicate spherical Zn coating.

Properties		MFZA paint	Traditional silicate spherical Zn coating
Liquid	Pigment content (mass%)	25	85
	Suspension property	No setting	Setting
Coating	Appearance	silver	Gray
	Thickness (µm)	~60	100
	Salt spray (h)	1200	1000
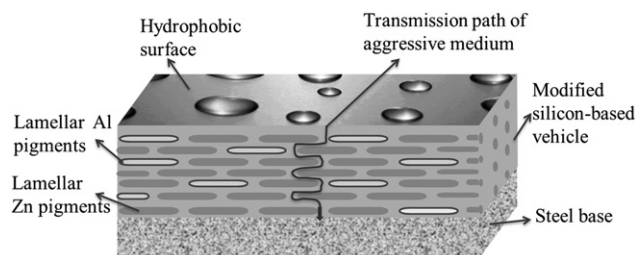
Fig. 10 Spatial structure model of anti-corrosion mechanism of the MFZA coating.

coating, its duration time to the salt spray is longer than that of the spherical Zn coating. It is obvious that the new produced MFZA coating is excellent quality and reasonable price.

3.6. Anti-corrosion model of the MFZA coating

The excellent corrosion resistance of the MFZA coating could be further explained by its spatial structure model, as shown in Fig. 10. In this model, the excellent effects of the potassium silicate modified by the silicon-acrylate emulsion could be described from three aspects. Firstly, the high wettability of the modified silicon-based vehicle of the lamellar pigments results in the improved compactness of the MFZA coating. Secondly, the brittleness of the MFZA coating is reduced due to the adding of the organic components. Furthermore, the hydrophobic effect of the MFZA coating is endowed by the modified silicon-based vehicle, which improves its water resistance.

In the MFZA coating model, the cathodic protection is from the electrical contact between the lamellar Zn (Al) pigments and the steel base. The lamellar pigments are overlapped in a parallel form, resulting in the prolonged path of corrosion medium and finally improving corrosion resistance. In addition, the current density between the pigments and the steel base is decreased due to the passivation of the lamellar Al pigments in the MFZA coating, which prolongs the cathodic protection period. Therefore, the synergetic action of the lamellar Zn (Al) pigments and the modified silicon-based vehicle brings the excellent corrosion resistance of the MFZA coating.

4. Conclusions

The potassium silicate solution vehicle was modified by the silicone-acrylic emulsion for improving wetting and dispersing of the lamellar Zn and Al pigments. The modified coating (MFZ coating) presented excellent performance, while the lamellar Zn pigments content could be reduced to 25 mass%.

In comparison with the unmodified coatings, MFZ coating presented improved adhesion grade, increased E_{corr} value, decreased anodic polarization current, more effective cathodic protection and higher acid resistance.

The waterborne Zn-rich coating with modified silicon-based vehicle, lamellar Zn and Al pigments exhibited better performances than the unmodified Zn-rich coating. The excellent performances of the MFZA coating arise from the synergistic effect of the potassium silicate and the silicon-acrylate emulsion with the lamellar Zn and Al mixture pigments. And the economic benefit and corrosion resistance of the new MFZA coating are superior to those of the traditional spheric Zn paint.

Acknowledgments

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